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Gas absorption in an agitated gas–liquid–liquid system

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Abstract

Gas–liquid–liquid systems have gained interest in the past decade and are encountered in several important industrial applications. In these systems an immiscible liquid phase may affect the gas absorption rate significantly. This phenomenon, however, is not completely understood and underlying mechanisms need further study. In this work the well-known Danckwerts-plot technique is used to determine the liquid side mass transfer coefficient k_L and the gas–liquid interfacial area a simultaneously in this type of systems. As absorption/reaction system CO_2 absorption in a 0.5 M K_2CO_3/0.5 M $KHCO_3$ buffer solution catalysed by sodium hypochlorite was chosen. Toluene, *n*-dodecane, *n*-heptane and 1-octanol were applied as dispersed liquid phases. The Danckwerts-plot could be well used in gas–liquid–liquid systems and from the results it appeared that two types of systems exist; systems that enhance mass transfer and systems that do not enhance mass transfer. Effects at low dispersed phase hold-up were observed to be very strong and are thus important, but were not taken into account in further analysis of the effect of dispersed phase hold-up on mass transfer. In systems where dodecane and heptane were added to the buffer solutions no enhancement of mass transfer was observed. However, the addition of toluene and 1-octanol caused an enhancement of mass transfer that could be well described using a homogeneous model of the shuttle mechanism.

Keywords: Mass transfer; Enhancement; Gas-liquid-liquid; Danckwerts-plot

1. Introduction

Gas–liquid–liquid systems have gained interest in the past decade due to the introduction of homogeneous biphasic catalysis in various reaction systems, e.g. hydroformylation, carbonylation, hydrogenation and oligomerization (Cornils, 1999). The main advantage of these systems over catalysis in one phase is the easy separation of the catalyst and the reactants or products. In this way advantages of homogeneous catalysis (no internal mass transfer limitations and often higher selectivities) and of heterogeneous catalysis (easy catalyst separation) can be combined. Important industrial applications are, e.g., the SHOP-process and hydroformylation of propene to butyraldehyde.

Gas–liquid–liquid systems are further encountered in reaction systems which inherently consist of three phases due to two (or more) immiscible reactants, reaction products or catalyst. For example, in the Koch reaction system all three reactants originate from different phases (Falbe, 1980). Gas–liquid–liquid systems are also encountered in areas in which an additional inert liquid phase is added on purpose to a gas–liquid system to increase the mass transfer rate. This latter concept is e.g. applied in a few biochemical applications (Rols, Condoret, Fonade & Goma, 1990). However, the addition of a second liquid phase can also retard the gas–liquid mass transfer (Yoshida, Yamane & Miyamoto, 1970).

In this latter perspective, especially when considering that the gas absorption rate is frequently the capacity determining factor, it is very important to understand the phenomena occurring in these systems for design and operation of these systems.

The gas absorption rate in stirred multiphase reactors is usually characterised by the volumetric mass transfer coefficient k_La. In this coefficient the liquid side mass transfer coefficient k_L as well as the interfacial area a are discounted.

To study the underlying phenomena of the effect of adding an immiscible liquid phase on the gas absorption rate for a gas–liquid system, it is considered necessary to separate the effects on the interfacial area a from those on the liquid side mass transfer coefficient k_L. In this work the Danckwerts-plot technique to measure k_L and a simultaneously by chemical absorption is used to study the

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effects of the addition of different immiscible organic phases. In this work four different gas–liquid–liquid systems will be studied.

2. Previous work

One of the first encounters in literature on gas–liquid–liquid systems is the work of Yoshida et al. (1970). In their work the oxygen absorption rate was measured in aqueous dispersions of a.o. kerosene and toluene. The observed effects on the addition of these dispersed phases were very different. The addition of kerosene resulted in a decrease of the volumetric mass transfer coefficient k_La. On the other hand, toluene caused, after a sharp initial decrease, a strong increase in the mass transfer rate at higher hold-ups.

Linek and Beneš (1976) studied gas absorption in liquid–liquid systems with a known value for the interfacial area to determine the influence on the liquid side mass transfer coefficient k_L. They studied oxygen absorption in aqueous emulsions with a mixture of *n*-alkanes and with oleic acid. The value of k_L remained practically constant in the presence of *n*-alkanes before phase inversion, while the addition of oleic acid caused an initial decrease of k_L. When more oleic acid was added, k_L increased again.

A few studies have been presented in literature on the influence of a second immiscible liquid on the gas–liquid interfacial area Mehta and Sharma (1971) used a fast reaction, CO_2–NaOH system, to study the influence of 2-ethyl-hexanol on the specific gas–liquid interfacial area. According to the authors the area increased due to a prevention of bubble coalescence. Das, Bandopadhyay, Parthasarathy and Kumar (1985) studied the interfacial area in gas–liquid–liquid systems with both a physical and a chemical method. As dispersed phases 2-ethyl-hexanol, toluene and methyl-isobutyl-ketone were used. All systems showed initially an increase in the interfacial area with higher dispersed phase fraction, but above approximately 10% hold-up the area started decreasing. The increase was explained by prevention of bubble coalescence, while a diminished level of turbulence in the reactor caused the decrease at higher hold-ups, according to the authors.

Several mechanisms have been proposed to explain the experimental results, thereby focusing on the gas absorption enhancement effect. In the literature actually two types of mechanisms were suggested. The first one is the so-called shuttle- or grazing mechanism, analogous to the one in gas–liquid–solid three phase systems. The mechanism is based on dispersed phase drops entering the mass transfer film at the gas–liquid interface to enhance mass transfer due to their higher solubility for the gas-phase component to be transferred. A homogeneous model describing this mechanism was proposed by Bruining, Joosten, Beenackers and Hofman (1986). They tested the model using oxygen absorption in aqueous solutions using *n*-hexadecane as a dispersed phase. Brilman, Goldschmidt, Versteeg and van Swaaij (2000) recently developed 3-D heterogeneous mass transfer models to study this grazing effect in more detail. From their overview of all models describing these effects, it can be concluded that, although these heterogeneous models are to be preferred from a physical point of view, the homogeneous models describe the experimental data equally well for simple cases and require less detailed input parameters.

The second mechanism proposed to describe the mass transfer enhancement is the so-called coalescence–redispersion mechanism, which is based on direct contact between gas and the dispersed phase by formation of gas–liquid complexes (Rols et al., 1990). The gas absorption rate is then enhanced due to the introduction of this second transfer path.

Concluding from experiments and models reported in the literature, it appears that there is a lot of confusion about the gas absorption mechanism and effects in gas–liquid–liquid systems. By studying experimentally the effects on k_L and a separately, more insight on the mechanism may be obtained.

3. Experimental technique

3.1. Danckwerts plot

For a better analysis of the observed effects on the mass transfer rate the simultaneous determination of the liquid side mass transfer coefficient k_L and the interfacial area a has been selected, using the well-known Danckwerts-plot technique (Danckwerts, 1970). The major advantage of this chemical absorption method over a physical absorption technique is that, when the reaction is fast enough, the bulk concentration of the dissolved gas is negligible, which implies that the driving force for mass transfer is well known. This allows for accurate determination of the mass transfer parameters k_L and a during stationary conditions. The determination of the interfacial area by physical measurement techniques in gas–liquid–liquid systems is also difficult to perform. The dispersions are often completely opaque, which implies that laser- and photographic techniques are difficult to use in these systems. Also the use of intrusive methods like a capillary technique to determine bubble sizes is not without severe complications in these systems. Non-representative sampling, coalescence and break-up during sampling and the disturbance of the flow pattern can be disadvantageous in these methods. By using the Danckwerts-plot technique a representative tank-averaged absorption rate is determined, circumventing above-mentioned difficulties.

According to the Danckwerts surface renewal model for mass transfer the rate of absorption for a reaction with negligible bulk concentration can be described as

$$R_A = k_L\sqrt{1 + Ha^2}c_{Ai\mathrm{L}}aV_L. \quad (1)$$

This equation holds when the gas side mass transfer resistance can be neglected. *Ha* is the Hatta number that is defined for a first- or pseudo-first-order reaction by

$$Ha = \sqrt{\frac{k_{\mathrm{Lapp}}D_A}{k_L^2}}. \quad (2)$$

From these equations it can be seen that by changing the value of the apparent rate constant k_{Lapp} a straight line can be obtained by plotting $(R_A/c_{Ai\mathrm{L}}V_L)^2$ versus $k_{\mathrm{Lapp}}D_A$. In this plot the slope is equal to a^2 and $(k_La)^2$ equals the intercept with the vertical axis. In this way k_L and a can be determined simultaneously.

3.2. System

As an absorption/reaction system carbon dioxide absorption in a 0.5 M potassium carbonate/0.5 M potassium bicarbonate buffer solution was used. This carbonate/bicarbonate buffer solution is the continuous liquid in the experiments done. As dispersed liquid phase several different organic liquids have been applied; toluene, *n*-dodecane, *n*-heptane and l-octanol. In the continuous liquid phase the following reactions occur:

$$\mathrm{CO_2} + \mathrm{H_2O} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{HCO_3} + \mathrm{H^+} \quad (3)$$

instantaneously followed by the equilibrium reaction:

$$\mathrm{CO_3^{2}} + \mathrm{H^+} \rightleftharpoons \mathrm{HCO_3}. \quad (4)$$

As a catalyst for reaction (3) sodiumhypochlorite is used. This allows for a wide variation of the reaction rate on addition of only small amounts of catalyst, so that the psycho-chemical parameters of the catalyst/buffer system do not change significantly. As catalytic species hypochlorite was chosen over arsenite because of its lower toxicity.

Due to the pH (≈ 10) also hydroxyl ions will be present in the buffer solution. Carbon dioxide reacts with $\mathrm{OH^-}$ according to the following reaction:

$$\mathrm{CO_2} + \mathrm{OH} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{HCO_3}. \quad (5)$$

The reaction rates for the reactions (3) and (5) are both first order with respect to $\mathrm{CO_2}$. Danckwerts (1970) has shown that under certain conditions, which are all fulfilled in this work, the reaction is pseudo-first order with respect to $\mathrm{CO_2}$ and the rate equation can be defined by

$$r_{\mathrm{CO_2}} = (k_3 + k_c c_{\mathrm{cat}} + k_5 c_{\mathrm{OH^-}})(c_{\mathrm{CO_2}} - c_{\mathrm{CO_2},e}). \quad (6)$$

In this equation $c_{\mathrm{CO_2},e}$ represents the equilibrium concentration of carbon dioxide, which depends a.o. on the carbonate and bicarbonate concentrations (Danckwerts, 1970). Under the experimental conditions the equilibrium concentration $c_{\mathrm{CO_2},e}$ is very small and can therefore be neglected. Eq. (6) can now be simplified to:

$$r_{\mathrm{CO_2}} = k_{\mathrm{Lapp}}c_{\mathrm{CO_2}} \quad \text{with } k_{\mathrm{Lapp}} = k_3 + k_c c_{\mathrm{cat}} + k_5 c_{\mathrm{OH^-}}. \quad (7)$$

Already at very low catalyst concentrations the catalysed reaction is dominant: $k_c c_{\mathrm{cat}} \gg k_3$ and $k_c c_{\mathrm{cat}} \gg k_5 c_{\mathrm{OH^-}}$. This means that the rate of reaction can be easily varied by changing the catalyst concentration.

The kinetics of the uncatalysed reaction ($k_3 \approx 0.02\ \mathrm{s^{-1}}$) were determined by Danckwerts and Sharma (1966). The value of k_5 is strongly dependent on ionic strength and the nature of the cations. k_5 was estimated to be $11.6\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$ using the work of Pohorecki and Moniuk (1988). Sharma and Danckwerts (1963) and Benadda, Prost, Ismaily, Bressat and Otterbein (1994) measured kinetic constants of the sodiumhypochlorite catalysed reaction in a 0.5 M $\mathrm{Na_2CO_3}$/0.5 M $\mathrm{NaHCO_3}$ buffer and in a 0.4 M $\mathrm{K_2CO_3}$/0.4 M $\mathrm{KHCO_3}$ buffer, respectively. Although the value of k_c depends on ionic strength and the counter ion of the buffer the values were not very different at 293 K. A value for k_c of $1.8\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$ (at 294 K) was used in the mass transfer calculations.

Nevertheless, for studying the effect of an immiscible liquid phase on the mass transfer coefficient k_L and a their absolute values are of minor importance, implying that the apparent reaction rate constants are known sufficiently accurate. In this work especially the relative changes in k_L and a will be studied.

The solubility of carbon dioxide in the buffer solution is estimated using the work of Weisenberger and Schumpe (1996):

$$\log\left(\frac{c_{G,0}}{c_G}\right) = \sum(h_i + h_G)c_i. \quad (8)$$

The value of $(c_{G,0}/c_G)$ was determined to be 1.57. The solubility of carbon dioxide and the diffusion coefficient in water were determined using correlations proposed by Versteeg and van Swaaij (1988):

$$He_{\mathrm{CO_2/H_2O}} = 3.59 \times 10^7 \exp\left(\frac{2044}{T}\right), \quad (9)$$

$$D_{\mathrm{CO_2/H_2O}} = 2.35 \times 10^6 \exp\left(\frac{-2119}{T}\right). \quad (10)$$

The diffusion coefficient of $\mathrm{CO_2}$ in the ($\mathrm{K_2CO_3/KHCO_3}$) buffer solution can be estimated by a correlation of Joosten and Danckwerts (1972) and was

estimated to be 1.5×10^{-9} m^2 s^{-1}:

$$\left(\frac{D_{CO_2/buffer}}{D_{CO_2/water}}\right) = \left(\frac{\mu_{water}}{\mu_{buffer}}\right)^{0.818}. \quad (11)$$

The viscosity of the buffer solution was estimated from the Handbook of Chemistry and Physics (1994).

3.3. Set-up

The set-up consists of a gas premix section, a reactor and an analysis section, which is schematically shown in Fig. 1. In the premix section the feed gas is composed using two mass flow controllers (one for CO_2 and one for N_2). The feed gas is introduced at the bottom of the stirred tank using a single orifice (1 mm). The unabsorbed carbon dioxide and nitrogen leave the reactor at the top. Condensable liquid components from the reactor are condensed in a cold trap. This cold trap consists of an ice bath at 273 K and a cryostat at 258 K. The CO_2-concentration is then analysed by an infrared analyser and recorded versus time by a personal computer.

The reactor is jacketed and has a working volume of 2.5 l and an inner diameter of 149 mm. The dispersions inside the reactor are agitated by a 6-bladed Rushton-turbine. The diameter of the turbine is 1/3 of the inner diameter of the tank and is placed 50 mm above the bottom of the reactor. Four baffles with a width of 15 mm ensure adequate mixing within the reactor. The pressure control in the reactor consists of a 1.5 m water column, which also serves as a sparge for the gas that is not led through the CO_2-analyser.

Experiments were carried out at a constant temperature of 294 K and a pressure of approximately 1.15 bars. Power input and total liquid volume were kept constant during all the experiments. The stirrer rate was approximately 1100 rpm in all the experiments. The different amounts of buffer solution and organic liquid phase were used batchwise in the reactor.

The inlet flow consisted of 1.70% carbon dioxide, which could be accurately determined (within 0.3%) by leading the gas directly to the CO_2-analyser. Gas absorption rate could be calculated by measuring the steady-state value of the CO_2 concentration in the outgoing flow. Depletion of CO_2 in the gas phase was always less than 70%, implying that the assumption of an ideally mixed gas phase does not influence the results.

The gas hold-up was determined using the liquid height before the gassing and an estimation of the height of the dispersions during the experiments.

The Danckwerts-plot technique was initially applied for the CO_2-buffer two-phase system to check the validity of the method and operating conditions. Subsequently, the same technique was used in the presence of toluene, *n*-heptane, *n*-dodecane and 1-octanol.

All chemicals used in this research were of high purity ($> 99\%$). Because sodiumhypochlorite solutions may decompose spontaneously, the hypochlorite concentration was determined before every experiment by standard iodometric titration.

4. Results and discussion

4.1. Danckwerts plots

Both for the CO_2–K_2CO_3/$KHCO_3$ two-phase system as well as for the systems in the presence of a dispersed organic liquid phase the Danckwerts plots showed excellent linearity, implying that this method can be used for determining the mass transfer coefficient and the interfacial area simultaneously. In Fig. 2 the Danckwerts plot for the CO_2–K_2CO_3/$KHCO_3$ two-phase system and an example of a plot for a system with a dispersed organic phase (20% dodecane) are presented.

4.2. Mass transfer parameters

The Danckwerts plots have been measured for each dispersed phase at different hold-ups on the organic liquids. In Fig. 3 the results are presented for the volumetric mass transfer coefficient, k_La, for every dispersed phase used as measured by the Danckwerts-plot technique.

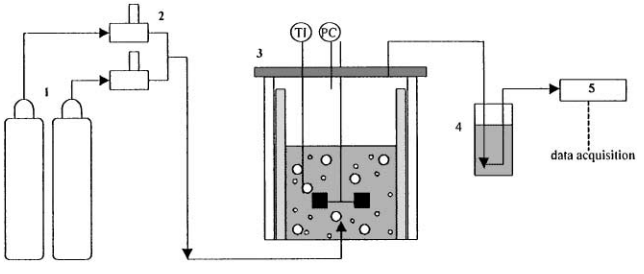

Fig. 1. Experimental set-up: 1: gas cylinders, 2: mass flow controllers, 3: reactor, 4: cold trap, 5: CO_2-analyser.

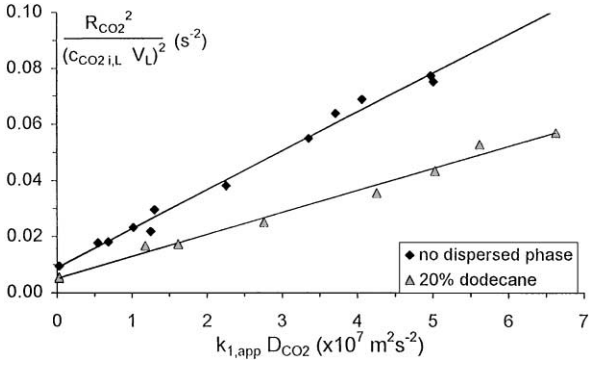

Fig. 2. Danckwerts-plot without a dispersed phase and in the presence of 20% *n*-dodecane.

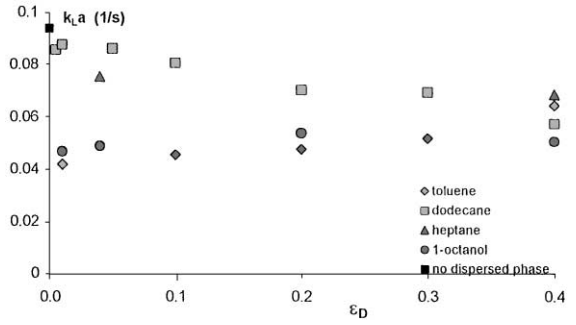

Fig. 3. Absolute k_La values for the four dispersed phases used.

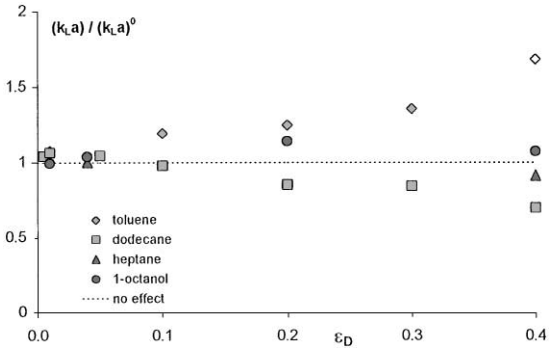

Fig. 4. Relative k_La values for the four dispersed phases used.

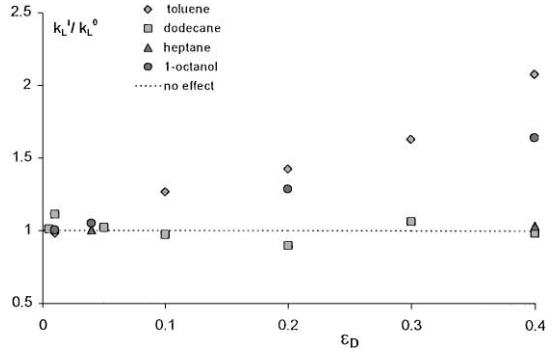

Fig. 5. Relative k_L values for the four dispersed phases used.

The initial decrease in k_La at low dispersed organic phase hold-ups is striking, as can be seen in Fig. 3. These initial effects are very strong in the case of toluene and 1-octanol and less pronounced with dodecane and heptane. From the results of the Danckwerts plots it was possible to determine both k_L and a. It was found that the initial decrease in k_La on the addition of toluene was completely due to a decrease in the interfacial area (a part of this decrease could be contributed to a decrease in the gas hold-up). The initial decrease in k_La with toluene as a dispersed phase was also observed by Yoshida et al. (1970) in their work on oxygen absorption in aqueous dispersions.

However, the initial decrease in k_La with the addition of 1-octanol was completely due to a decrease in the value of the mass transfer coefficient k_L, and are probably due to changes in the surface chemistry of the system (surface tension and the formation of semi-rigid boundary layers). Analogous results were also observed by Eckenfelder and Barnhart (1961) in their work on the influence of surfactants (to which 1-octanol can also be accounted for) on mass transfer.

As the scope of this work is to study the influence of adding a dispersed phase on the mass transfer rate, the initial effects are important. However, to be able to compare the results for the four dispersed phases used at higher organic phase hold-ups the initial effects should not be taken into account. In Fig. 4 the relative values for k_La are presented for the organic phases used. The relative value of k_La is defined by the ratio of the absolute value of k_La at higher hold-ups to the value obtained from extrapolation to zero hold-up.

From Fig. 4 it can be seen that the relative values of k_La increase on addition of toluene. The addition of 1-octanol caused a slight increase up to 20% organic phase and at 40% 1-octanol the increment was somewhat lower. The addition of dodecane (and heptane) caused a decrease in the mass transfer rate. Despite the fact that all organic dispersed phases used have a higher physical solubility for carbon dioxide when compared to the aqueous buffer solution, two types of systems appear to exist; one that enhances mass transfer and one that retards mass transfer. This effect was also observed by Yoshida et al. (1970, see Section 2). In their work the addition of kerosine, which is in fact comparable to dodecane, retarded mass transfer and the addition of toluene-enhanced mass transfer (after a sharp initial decrease).

The effects on the relative values of the mass transfer coefficient k_L as determined from the Danckwerts-plots are presented in Fig. 5, showing that the relative value of k_L as calculated from the Danckwerts-plots increased on the addition of toluene and 1-octanol. When dodecane and heptane were added to the buffer solutions the liquid side mass transfer coefficient remained practically constant.

In Fig. 6 the relative values of the interfacial area are plotted versus the fraction dispersed organic phase in the reactor. The value decreased with the addition of 1-octanol and toluene. The relative value of the gas–liquid interfacial area remained approximately constant up to 20% dodecane. Beyond this value, the area started also decreasing.

4.3. Interpretation

When a dispersed phase is present in the reactor it is very important that the values for the mass transfer parameters which are obtained from the Danckwerts

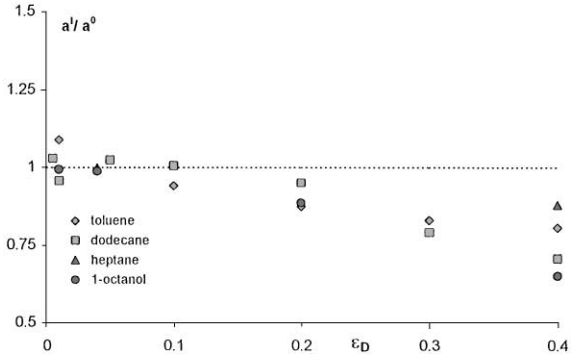

Fig. 6. Relative values of the interfacial area for the four dispersed phases used.

plots are analysed correctly. In the absence of a second liquid phase the rate of absorption is described by Eq. (1), as is confirmed by the linearity of the Danckwerts plot (Fig. 2). Droplets with a higher solubility for the gas phase component to be transferred, however, may change the concentration profile within the mass transfer zone at the gas–liquid interface (if the droplets are actually present in that zone). To describe the rate of absorption in this latter situation a homogenous model of the shuttle mechanism (Section 2) was used. This model was chosen to determine if the presence of immiscible dispersed phase droplets within the mass transfer zone could explain the observed effects on the gas–liquid absorption rates measured and on the corresponding mass transfer parameters k_L and a as determined by the Danckwerts-plot technique.

When using a homogeneous model of the shuttle mechanism for the description of the absorption process, implicitly a few assumptions are made:

1. The dispersed phase is equally divided throughout the gas–liquid mass transfer zone.
2. The concentration of carbon dioxide in the dispersed phase is at any time and place within the mass transfer zone at equilibrium with its concentration in the surrounding continuous phase.
3. The presence of the microphase droplets does not influence the surface renewal frequency of the continuous liquid phase.

The second assumption implies that liquid–liquid mass transfer resistance is neglected, which may not necessarily be true. The liquid–liquid mass transfer coefficient depends a.o. upon the diffusion coefficients and the diameter of the droplets. Detailed information on these parameters was not available for the system under consideration.

According to the Danckwerts surface renewal model the concentration profile of a gas-phase component A, that is being absorbed in a liquid containing microphase droplets within the mass transfer zone, can be described by Eq. (12), assuming a first-order reaction in the continuous phase:

$$D_A \frac{\partial c_A^2(x,t)}{\partial x^2} = k_L(1-\varepsilon_D)c_A(x,t) + (1+\varepsilon_D(m_R-1))\frac{\partial c_A(x,t)}{\partial t} \quad (12)$$

with boundary conditions

$$t=0,\ x>0: \quad c_A(x,t) = c_{A,\mathrm{bulk}}, \quad (13)$$

$$t>0,\ x=0: \quad c_A(x,t) = c_{A\mathrm{iL}}, \quad (14)$$

$$t>0,\ x=\infty: \quad c_A(x,t) = c_{A,\mathrm{bulk}}. \quad (15)$$

When the capacity of the liquid bulk is sufficient, the concentration of the gas in the bulk can be assumed zero; $c_{A,\mathrm{bulk}} = 0$. Equation (12) can now be solved analytically and the flux through the gas–liquid interface, according to the Danckwerts surface renewal model, is given as

$$R_A = k_L\sqrt{1+\varepsilon_D(m_R-1)+(1-\varepsilon_D)Ha^2}\,c_{A\mathrm{iL}}aV_L. \quad (16)$$

The Hatta number is defined in Eq. (2). Now it is possible to define an enhancement factor for the presence of a dispersed phase and a first-order reaction in the continuous phase according to a homogeneous model of the shuttle-mechanism. The enhancement factor E_D in Eq. (17) is the ratio of the flux in Eq. (16) and the flux in case there is no dispersed phase present ($\varepsilon_D = 0$):

$$E_D = \frac{R_A(\varepsilon_D \neq 0)}{R_A(\varepsilon_D = 0)} = \sqrt{\frac{1+\varepsilon_D(m_R-1)+(1-\varepsilon_D)Ha^2}{1+Ha^2}}. \quad (17)$$

As is shown in Eq. (16) there is a difference in the interpretation of the Danckwerts plot when there are no dispersed phase drops present in the mass transfer region (case I) and when there are (case II). When the results of the gas absorption measurements are plotted as explained in Section 3.1, $(R_A/c_{A\mathrm{iL}}V_L)^2$ versus $k_{\mathrm{Lapp}}D_A$, the intercept with the vertical axis and the slope of the Danckwerts plot can be interpreted as shown in Table 1.

Analysis of the mass transfer parameters for the different organic liquid-phase fractions in the reactor showed two different effects for the dispersions used in this research. The addition of toluene and 1-octanol caused an increase in the value of the mass transfer coefficient when case I is applied for analysis of the Danckwerts plot, like is done in Fig. 5. However, this k_L value remained prac-

Table 1
Interpretation of the Danckwerts plot

	Case I	Case II
Slope	a^2	$a^2(1-\varepsilon_D)$
Intercept	$(k_La)^2$	$(k_La)^2.\ (1+\varepsilon_D(m_R-1))$

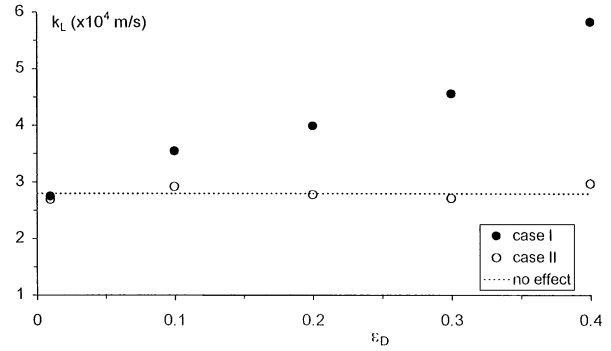

Fig. 7. k_L versus toluene hold-up when both case I and case II are assumed.

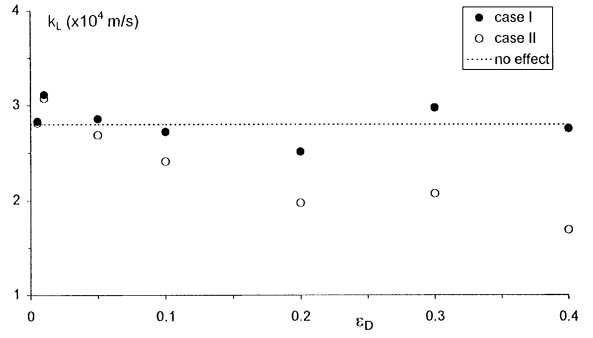

Fig. 8. k_L versus dodecane hold-up when both case I and case II are assumed.

tically constant in case II, when assuming organic drops to be present within the mass transfer zone enhancing absorption rate. The value of k_L was expected to remain practically constant, because this value mainly depends on power dissipation and hydrodynamic conditions, which could be assumed constant in all experiments. In Fig. 7 the dependence of k_L on the toluene fraction is presented when cases I and II are assumed.

From Fig. 7 it appears that the Danckwerts plot in the presence of toluene and 1-octanol is probably best interpreted using case II. Mass transfer in these systems is then enhanced by the addition of a dispersed phase and the surface renewal frequency is constant and thus not influenced by the dispersed phase droplets.

However, with dodecane and heptane as dispersed phases a completely different effect was observed. When case I was chosen for the interpretation of the Danckwerts plot the value of k_L remained at a constant level, while under case II the value decreased with increasing fraction of dispersed phase. In Fig. 8 an example of this effect is shown with dodecane as the dispersed phase.

From Fig. 8, and the fact that mass transfer is not enhanced by dodecane or heptane (see Section 4.2), it can be concluded that for these systems no dispersed phase is likely to be present in the mass transfer region and case I is favored to interpret the mass transfer parameters.

The mass transfer parameters k_L and a as determined from the Danckwerts plots when case II is applied are presented in Figs. 9 and 10.

The results indicate that probably two types exist within the four of gas–liquid–liquid systems studied. In this work an enhancement of mass transfer was observed (when initial effects are discarded) with increasing amounts of toluene and 1-octanol added to the buffer solutions. The addition of dodecane and heptane, however, caused a decrease of mass transfer.

For the addition of toluene and 1-octanol the effects on k_L can be explained best when assuming dispersed droplets to be present in the mass transfer zone (case II, see Fig. 9). The value of k_L^{II}/k_L^0 now remains practically constant as was expected for constant power dissipation.

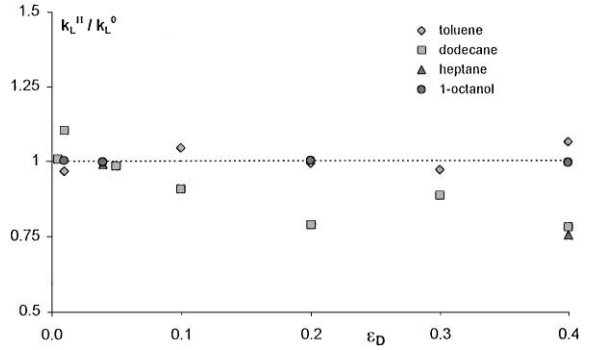

Fig. 9. k_L/k_L^0 versus dispersed-phase hold-up when case II is assumed.

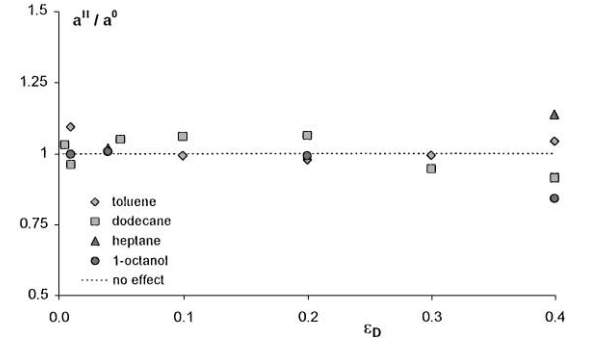

Fig. 10. a/a^0 versus dispersed phase hold-up when case II is assumed.

In Fig. 11 the data of Fig. 5 are re-plotted together with the model predictions for the shuttle mechanism. When using a Case I Danckwerts' plot interpretation for a situation in which droplets are present within the mass transfer zone, the apparent k_L^I coefficient is described by (see Table 1)

$$\frac{k_L^1}{k_L^0} = \sqrt{\frac{1+\varepsilon_D(m_R-1)}{1-\varepsilon_D}}. \tag{18}$$

The value for the interfacial area, after accounting for initial effects, remains constant up to at least 20% organic phase hold-up (Fig. 10).

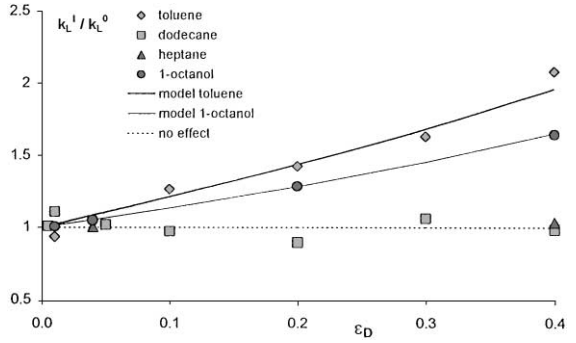

Fig. 11. Relative values for k_L when case I is applied. The model lines represent the enhancement factor as determined from the model.

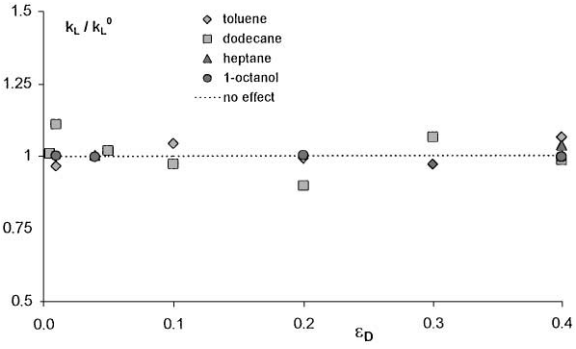

Fig. 12. Interpreted k_L values.

The experimental results of dodecane and heptane dispersions, however, are best described assuming no dispersed phase in the mass transfer zone (case I). The value of the mass transfer coefficient then remained practically constant (as expected) and in dodecane dispersions the interfacial area was constant up to 20% dispersed phase fraction and then started decreasing (Fig. 6). In Fig. 11 the absence of mass transfer enhancement is clearly shown.

When applying the most probable situations for each of the gas–liquid–liquid systems studied (thus: case I for dodecane and heptane and case II for toluene and 1-octanol) the resulting k_L values are plotted in Fig. 12. For a/a_0 the value remained constant in all cases up to 20%.

If this interpretation is valid (which needs further validation), these results show that the surface renewal frequency in these multiphase systems is not influenced by the presence of dispersed phase droplets.

5. Conclusions

The Danckwerts-plot technique was used for analysis of mass transfer parameters in gas–liquid–liquid systems. From the experimental results and by interpretation of the Danckwerts plots the existence of two types of gas–liquid–liquid systems is indicated. Mass transfer is enhanced due to the addition of toluene and 1-octanol to aqueous buffer solutions, which could be well described by a homogeneous model of the shuttle mechanism. Addition of *n*-dodecane and *n*-heptane, however, causes no enhancement of mass transfer. Initial effects (at low dispersed phase fraction) can be very strong and further study on these effects is required.

To validate the conclusions drawn from the experimental results in this work for the effect on the mass transfer parameters k_L and a, independent physical measuring techniques will be developed.

Notation

a	gas–liquid interfacial area, m^2/m^3 liquid
c_A	concentration of component A, mol m^{-3}
c_{AiL}	concentration of component A at the gas–liquid interface, mol m^{-3}
D_A	diffusion coefficient of component A, $m^2\ s^{-1}$
E_D	enhancement factor due to the dispersed phase, dimensionless
Ha	Hatta number, defined in Eq. (2), dimensionless
He	Henry's law constant, mol m^{-3} Pa^{-1}
h_i, h_G	parameters in Eq. (8), m^3 mol^{-1}
k_{Lapp}	apparent first-order rate constant, s^{-1}
k_{-3}, k_3	reverse and forward reaction rate constant of reaction (3), s^{-1}
k_{-5}, k_5	reverse and forward reaction rate constant of reaction (5), $m^3\ mol^{-1}\ s^{-1}$
k_c	rate constant of the catalysed reaction (3), $m^3\ mol^{-1}\ s^{-1}$
k_L	liquid side mass transfer coefficient, m s^{-1}
m_R	ratio of the gas solubility in the dispersed and in the continuous phase, dimensionless
r_A	reaction rate of component A, mol $m^{-3}\ s^{-1}$
R_A	rate of absorption of component A, mol s^{-1}
T	temperature, K
V	volume, m^3

Greek letters

ε_D	dispersed phase fraction, dimensionless
μ	viscosity, Pa s

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